

# PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

### Fuel Cells

5 We, TOKYO SHIBAURA ELECTRIC COMPANY LIMITED, a Japanese corporate body, of 72 Horikawa-cho, Kawasaki-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a hydrogen-oxygen fuel cell using as fuel the hydrogen obtained by decomposing methanol.

15 It is already known that hydrogen is the most useful fuel for a fuel cell. In general, a hydrogen-oxygen fuel cell consists of an electrolyte solution such as an aqueous alkaline solution, a pair of porous electrodes each carrying a catalyst, disposed opposite each other with the electrolyte solution between them, and two chambers formed on the outside of the electrode assembly to hold hydrogen and oxygen or air respectively. The hydrogen gas in the hydrogen chamber, under atmospheric or increased pressure, permeates through the porous electrode in contact therewith, causing the known electrode reaction with the electrolyte. The oxygen gas in the oxygen chamber, under atmospheric or increased pressure, passes through the porous electrode exposed thereto, similarly causing the known reaction with the electrolyte. As a result, an electromotive force is created between the electrodes, and at the same time water is produced in the electrolyte solution.

35 For the continuous operation of the hydrogen-oxygen fuel cell, hydrogen and oxygen must be supplied in sufficient amounts to make up for consumption and the water produced by the electrode reaction must be removed from the electrolyte solution so as to

maintain the electrolyte at the proper constant concentration.

The present invention provides a fuel cell system including: a fuel cell comprising a non-porous hydrogen-permeable hydrogen electrode composed of palladium or an alloy thereof with at least one element from Group Ib of the Mendeleev Periodic Table, which electrode carries on one side a catalyst of palladium black and on the other side a catalyst comprising a mixed black of an alloy of palladium with platinum and/or rhodium, a hydrogen chamber at the said one side of the hydrogen electrode, an electrolyte chamber at the said other side of the hydrogen electrode which electrolyte chamber is packed with a matrix of alkali-resistant fibrous material which matrix is impregnated with alkaline electrolyte, a porous oxygen- and water-permeable oxygen electrode parallel to the hydrogen electrode, the said electrodes being at opposite sides of the electrolyte chamber, the oxygen electrode consisting of an alkali-resistant metal screen carrying a catalyst consisting of a black of a metal from Group VIII of the Mendeleev Periodic Table, and the oxygen electrode having on its surface remote from the electrolyte chamber a thin water-repellent porous film and an oxygen chamber at the side of the oxygen electrode remote from the electrolyte chamber; a hydrogen generator which comprises means for catalytic decomposition of methanol, means for separating from each other hydrogen and carbon monoxide produced by said decomposition, means for conveying the separated hydrogen to the hydrogen chamber, and means for burning the carbon monoxide to heat the said means for decomposition and the fuel cell; means for supplying oxygen to

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the oxygen chamber; and means for discharging from the oxygen chamber excess oxygen and water vapour entrained thereby.

In the fuel cell according to this invention, the water produced in the electrolyte solution with the progress of the electrode reaction permeates through the porous oxygen electrode and is entrained with the oxygen gas flowing through the oxygen chamber and then removed from the cell. Therefore, the electrolyte solution is always maintained at the proper constant concentration without the necessity of circulating it for additional concentration. Circulation of the oxygen gas is far easier than circulation of the electrolytic solution for concentration. Moreover, if the moist oxygen gas from the cell is reused after dehumidifying, there is no loss of oxygen gas.

In the accompanying drawing:

Figure 1 is a diagrammatic longitudinal sectional view of a fuel cell system according to the present invention; and

Figure 2 is an enlarged longitudinal partial section of the cell body used in the cell of Fig. 1.

The cell body 1 is housed in a sealed vessel 2, contained in a heating tank 7 having a gas inlet 3 on the underside, a gas outlet 4 at the top and a pair of electrical output terminals 5 and 6. The cell body 1 has a pipe 8 to supply hydrogen gas thereto, a pipe 9 to supply oxygen gas thereto, a pipe 10 to remove excess oxygen gas therefrom and a pipe 12 provided with a valve 11 at the end to remove air from the hydrogen chamber; these pipes penetrate through the walls of the heat retaining vessel 2 and the heating tank 7. The vessel 2 has a methanol chamber 13 outside the cell body 1. A pipe 15 leads from a point above the level of the methanol contained in the methanol chamber 13 and is provided with a pressure gauge 14 to check the pressure at which methanol vapour released is conducted to a means 16 for generating hydrogen gas.

The hydrogen generator 16 consists of an airtight cylindrical shell 17, a cylindrical body 18 disposed coaxially with the shell 17 in a manner to penetrate therethrough, and a tube 19 wound spirally about the circumferential surface of the cylindrical body 18. The wall of spiral tube 19 consists of a material permitting hydrogen gas to permeate through the wall thereof, for example, palladium or alloys of palladium and copper, silver or gold. The inner surface of the spiral tube 19 carries a catalyst of palladium black for thermal decomposition of methanol, and the outer surface thereof has a layer of catalyst to convert nascent hydrogen into a molecular form, e.g. a mixed black containing palladium and elements from group VIII in the Mendeleev periodic table. One end of the spiral tube 19 communicates with pipe 15 and the other end thereof is connected to a pipe 20 to lead

carbon monoxide remaining in the spiral tube 19 to the outside of the system. The pipe 20 is preferably connected through a valve 21 to a burner 22 disposed within the cylindrical body 18 to heat the cylindrical body 18 and the heating tank by burning the carbon monoxide. The interior of the shell 17 communicates with one end of the pipe 8, which is provided with a pressure gauge 23, so as to feed the hydrogen gas from the shell 17 to the cell body 1.

To the pipe 9 there is connected through a heat exchanger 24 a vessel 25 of oxygen gas, or preferably liquid oxygen. The pipe 10 is connected to the heat exchanger 24 to condense the water vapour contained in the moist oxygen gas flowing through the pipe 10, then to a trap 26 to remove condensed water from the gas, and finally to the pipe 9 through a blower 27 to supply the dried oxygen gas to the pipe 9 at the desired flow rate. There is also provided a pipe 28 to carry outside the system the water separated from the oxygen gas in the trap 26.

As illustrated in Fig. 2, the cell body 1 consists of a plurality of, for example thirteen, cell elements housed in a case 30. Each cell element comprises a hydrogen chamber 31, a non-porous hydrogen electrode 32, an electrolyte chamber 33, a porous oxygen electrode 34 and an oxygen chamber 35 arranged in the order mentioned. Adjacent cell elements are of exactly the same construction, except for the reversed order of arrangement, the hydrogen chambers 31 and oxygen chambers 35 being used in common to adjacent cells. The individual hydrogen chambers 31 are connected to said hydrogen supply pipe 8 through a bore 37 of an insulating packing 36 provided at the top of each chamber. The bottom of said hydrogen chamber is connected similarly through a bore 39 of an insulating packing 38 to the pipe 12, a valve 11 of which is normally closed. Each oxygen chamber 35 is connected at the top to the pipe line 9 through a bore 41 of an insulating packing 40 and at the bottom through a bore 43 of insulating packing 42 to the pipe 10 to discharge excess oxygen.

The non-porous hydrogen electrode 32 consists of an extremely thin substrate, for example, 0.01 to 0.05 mm, which is of palladium or an alloy consisting of palladium and copper, silver or gold, and is capable of allowing hydrogen gas to permeate there-through. The substrate carries layers of palladium black catalyst deposited on the side thereof facing the hydrogen chamber, and layers of mixed black catalyst containing palladium and platinum and/or rhodium deposited on the other side. This hydrogen electrode permits the permeation of hydrogen gas and satisfactorily catalyses the electrode reaction between hydrogen and the electrolyte.

The oxygen electrode 34 consists of a screen of alkali-resistant material having pores which have a diameter large enough to allow moisture to pass. The screen may be a nickel screen having openings of 0.08 to 0.3 mm. Particulate catalyst is deposited on said screen, being composed of black at least one element from group VIII of the periodic table or a mixture of such black and carbon. A porous film of polytetrafluoroethylene (P.T.F.E.) is formed on the side of the screen facing the oxygen chamber. The porous P.T.F.E. film may be prepared, for example, by spraying over the screen a dispersion of fine particles of P.T.F.E. in water at the rate of 0.05 to 0.5 mg/cm<sup>2</sup>, followed by sintering at temperatures of about 400°C. The P.T.F.E. film thus formed will allow restricted passage of moisture owing to its high water repellency. If a film deposited on the screen is composed of other substances than P.T.F.E., for example, polyethylene, polypropylene, and paraffin, the film tends to be decomposed or denatured by alkali and/or heat when the fuel cell is used under such conditions that the film is brought into contact with the alkaline electrolyte solution at relatively high temperatures.

Each non-porous hydrogen electrode 32 is connected through a conductor 44 to the terminals 5 and each porous oxygen electrode is connected through a conductor 45 to the other terminal 6.

The electrolyte chamber 33 is filled with an alkali-resistant fibrous matrix, e.g. glass fibres, asbestos or nylon fibres, which is impregnated with an electrolyte solution.

In operation, methanol is introduced into the methanol chamber 13 and the heat retaining vessel 2 is heated to 60 to 120°C, preferably to about 80°C, for example by introducing heated gas into the heating vessel 7 through the heated gas inlet 3. Thus the methanol in chamber 13 is vaporised, and vapour is transferred through the pipe 15 to the hydrogen generating means 16.

In the hydrogen generating means 16, the methanol vapour passes through the spiral tube 19 heated by the burner 22 installed within the cylindrical body 15 and is decomposed in contact with the palladium black catalyst deposited on the inner surface of the spiral tube 19, thus producing hydrogen and carbon monoxide. This decomposition of methanol will be effectively carried out when the methanol vapour contacts the catalyst at temperatures of 300 to 350°C. Beyond 350°C, by-product methane will be produced in increasing proportions, reducing the generation of hydrogen accordingly. The hydrogen produced by diffusion through the walls of the spiral tube 19 and reaches the free space within the shell 17. While penetrating through the tube, part of the hydrogen which remains in a nascent state is brought into contact with

the mixed black catalyst and is thus formed into stable hydrogen molecules.

The hydrogen gas within the shell 17 then flows through the pipe 8 into the hydrogen chamber 31. The pressure of the hydrogen gas in the hydrogen chamber is indicated by the pressure gauge 23.

Carbon monoxide, the other product of catalytic decomposition of methanol, is separated from the hydrogen and remains in the spiral tube 19 and is transferred at a controlled flow rate through the pipe 20 to the burner 22, where it is burnt to heat the cylindrical body 18, the combustion gases enter the heating device 7 through the inlet 3 and flow through the heating device 7, heating the heat retaining vessel 2 through its circumferential walls, and are finally released from the system through the exhaust 4.

The liquid oxygen contained in the liquid oxygen vessel 25 is vapourised by being heated in the heat exchanger 24. The oxygen gas thus evolved is conducted through the pipe 9 to the oxygen chambers of the cell body 1. The flow rate of oxygen gas to the oxygen chambers is required, for the reason discussed later, to be in excess of the amount of oxygen consumed by the reaction at the oxygen electrode.

In the cell body, the hydrogen gas reacts with the electrolyte at the surface of the non-porous hydrogen electrode 32 adjacent to the hydrogen chamber 31. The oxygen gas reacts with the electrolyte at the surfaces of the porous oxygen electrode 34. As a result of these reactions an electromotive force is created between the electrodes and at the same time water is produced in the electrolyte. The water thus produced permeates in the vapour phase through the oxygen electrode and is entrained in the form of vapour with the oxygen gas flowing through the oxygen chamber 35. If the same amount of water as that produced by the electrode reaction is removed from the surface of the oxygen electrode 34, the concentration of the electrolytic solution will obviously be maintained constant. The rate of evaporation of the water depends on the flow rate of the oxygen gas along the surface of the oxygen electrode 23 and the temperature of the water and oxygen gas. A suitable temperature for satisfactory operation of the fuel cell is generally from 60 to 120°C; water will then be evaporated and removed at the rate at which it is produced in the electrolyte, if oxygen gas is supplied in volumes 3 to 8 times those consumed in the reaction.

The oxygen gas which has been moistened due to part of the gas consumed in the electrode reaction being replaced by water vapour is conducted through the bore 43 of the packing 42 to the pipe 10, and, while passing through the heat exchanger 24, is

reduced in temperature by heating the oxygen supplied from the liquid oxygen vessel 25. By this cooling the vapour contained in the moistened oxygen gas is condensed, and the condensed water is separated from the oxygen gas while passing through the trap 26. The dried oxygen gas is supplied by the blower 27 for reuse. After the cell operation has attained the steady state it is only necessary to supply from the liquid oxygen vessel 25 oxygen gas to replace the amount consumed by the reaction.

Where the oxygen gas to be supplied contains other gases, the supply of said gas mixture is determined in such a manner that at least the required amount of oxygen for the electrode reaction is supplied and that the removal of water is fully effected. Since, in such a case, the gas released from the oxygen chamber contains reduced proportions of oxygen, it may be passed to waste. If atmospheric oxygen is used for supply to the fuel cell it will be possible to eliminate oxygen storage.

When hydrogen gas is charged into the hydrogen chamber at a pressure of one atmosphere, pure oxygen is continuously supplied to the oxygen chamber in amounts eight times those consumed in the electrode reaction, and operation is carried out at a temperature of 80°C, then the output from each cell element will be 100 mA/cm<sup>2</sup> and 84 mW/cm<sup>2</sup> at a voltage of 0.8 V. This is a much larger value than the output of 10 to 12 mW/cm<sup>2</sup> obtained with the same type of prior art fuel cell. When the fuel cell of the present invention is in normal operation, about 6 litres of methanol will produce an output of 15 KWh. The capacity of a vessel to hold this amount of methanol will be only about one seventh that of a vessel to contain sufficient amounts of hydrogen gas to produce the same output.

#### WHAT WE CLAIM IS:—

1. A fuel cell system including: a fuel cell comprising a non-porous hydrogen-permeable hydrogen electrode composed of palladium or an alloy thereof with at least one element from Group Ib of the Mendeleev Periodic Table, which electrode carries on one side a catalyst of palladium black and on the other side a catalyst comprising a mixed black of an alloy of palladium with platinum and/or rhodium, a hydrogen chamber at the said one side of the hydrogen electrode, an electrolyte chamber at the said other side of the hydrogen electrode which electrolyte chamber is packed with a matrix of alkali-resistant fibrous material which matrix is impregnated with alkaline electrolyte, a porous oxygen- and water-permeable oxygen electrode parallel to the hydrogen electrode, the said electrodes being at

opposite sides of the electrolyte chamber, the oxygen electrode consisting of an alkali-resistant metal screen carrying a catalyst consisting of a black of a metal from Group VIII of the Mendeleev Periodic Table, and the oxygen electrode having on its surface remote from the electrolyte chamber a thin water-repellent porous film, and an oxygen chamber at the side of the oxygen electrode remote from the electrolyte chamber; a hydrogen generator which comprises means for catalytic decomposition of methanol, means for separating from each other hydrogen and carbon monoxide produced by said decomposition, means for conveying the separated hydrogen to the hydrogen chamber, and means for burning the carbon monoxide to heat the said means for decomposition and the fuel cell; means for supplying oxygen to the oxygen chamber; and means for discharging from the oxygen chamber excess oxygen and water vapour entrained thereby.

2. A fuel cell system as claimed in claim 1 in which the discharging means includes a condenser arranged to be traversed by the excess oxygen and entrained water vapour for condensing the water vapour, a trap for separating the condensed water from the oxygen, and a pipe for returning the dried oxygen from the trap to the oxygen chamber.

3. A fuel cell system as claimed in claim 1 or 2 in which the oxygen supply means includes a liquid oxygen container, heating means for vapourising liquid oxygen from the container, and a pipe for conducting the vapourised oxygen from the heating means to the oxygen chamber.

4. A fuel cell system as claimed in claim 1, 2 or 3 in which the hydrogen generator includes an airtight vessel having an outlet pipe leading to the hydrogen chamber; a cylindrical tubular body extending through the vessel; a tube wound spirally about the exterior of the said body the tube having a hydrogen-permeable wall made of palladium or an alloy thereof with copper, silver, or gold, carrying on its internal surface a palladium black catalyst for decomposition of methanol and on its external surface a mixed black catalyst containing palladium and at least one element from Group VIII of the Mendeleev Periodic Table for converting nascent hydrogen to molecular hydrogen; methanol supply means connected to one end of the tube; and a carbon monoxide outlet at the other end of the tube connected to the burner, which burner is disposed in the tubular body.

5. A fuel cell system as claimed in claim 4 in which the fuel cell is housed in a vessel above the hydrogen generator which vessel is arranged to receive combustion gases from the tubular body.

6. A fuel cell system as claimed in claim 5 in which a methanol container connected to

said one end of the tube is disposed in the said vessel.

7. A fuel cell system substantially as herein described and shown in the accompanying

5 drawing.

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